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VARIATIONS IN REFRACTIVE INDEX OF CO_2-FREE DRY AIR AND A STATISTICAL CORRELATION WITH SOLAR ACTIVITY [1]

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ABSTRACT

Existing data on refractive indices of dry air as measured by various observers show disagreements larger than the errors that seem probable in many of the recent measurements. Chemical (volumetric) data relating to the constancy of composition of the atmosphere at the earth's surface do not suggest that any appreciable variations in refractivity should be found, but gravimetric data show small variations that have never been satisfactorily explained.

All refractive-index data taken on air since 1857 have been examined for evidences of systematic variations and a correlation between refractivity and annual sunspot number has been found, the Pearson r being -0.48 (± 0.08 probable error) as determined from 40 pairs of values.

Degree of storminess of the earth's atmosphere has already been (positively) correlated with yearly relative sunspot number and thus it seems possible that a decrease in the average rate of stirring and mixing of the air, such as occurs during times of low sunspot numbers, allows certain denser components (perhaps associated molecules or isotopes) to settle and produce at the earth's surface a gaseous mixture having a slightly higher index of refraction. In addition to simple sunspot periodicity of 11 years, however, a superimposed 23-year periodicity, corresponding to a magnetic cycle of sunspots, also seems indicated.

Although the value $\mu = 1.0002925$ at 0 C and 760 mm pressure is a fair general average for the sodium lines index of air, it appears unsafe to rely implicitly on the constancy of μ over a period of years. It may be preferable to make estimates from the equation $(\mu_D - 1) \times 10^7 = 2932.2 - 0.15\, S$, where S is the relative annual sunspot number, and the constants are provisional values derived from all available data. Further experiments should precede the adoption of any radiation in air as a standard of length.

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[1] In this investigation of possible periodicity in the refractive index of air, sunspot numbers are employed primarily as a well-known comparison standard of established periodicity that in an empirical manner is found suitable for use in making a numerical estimate of the probability that certain discrepancies among published indices of air are, or are not, the result of chance or accidental error. Far from implying a causal relation, a correlation coefficient can, of course, indicate nothing about the nature of a relationship or even show whether it is direct or indirect. The correlation of a phenomenon with sunspot numbers permits a rough pseudo comparison with a number of other phenomena that also have been correlated with such numbers, and these rough comparisons or associations in thought serve to suggest partial explanations which may lead to fruitful experiments.

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I. INTRODUCTION

In previous papers [2] discussing the errors of refractive-index measurement attention has been confined almost exclusively to goniometry and to other geometrical considerations. In these it has thus been assumed that the velocity of light in any given medium has a constant value for a given wave length, whether measurements are made simultaneously or follow after successive time intervals and whether the observations are made along the same or different paths. This, of course, can be true only when all pertinent physical and chemical conditions are well understood and under complete control.

It has long been assumed that our knowledge of the earth's atmosphere and its properties is sufficiently complete to justify the making of precise optical measurements in CO_2-free dry air. However, in view of the very high precision that is currently sought, and since certain small but definite variations have been found in the apparent weight of a normal liter of CO_2-free dry air, it is evident that a comprehensive survey of refractive-index errors should include careful consideration of possible variations in the composition and constitution of the atmosphere. Three well-known types of measurement that are frequently made on air and which have a direct bearing on this question are (1) density determinations, (2) chemical (chiefly volumetric) analyses, and (3) refractive-index determinations. Evidence from all three of these sources will be summarized before proceeding to a general discussion of interrelationships and possible periodic tendencies among variations in the properties of air.

II. GRAVIMETRIC EVIDENCE OF VARIATION

Approximately 50 years' work in precise weighings shows that observed densities of standard air are not as constant as similar results obtained by the same observers on certain other gases. Because of this lack of constancy in the normal density of air, the specific gravities of gases are now given in the Landolt-Börnstein Physikalisch-Chemische Tabellen [3] as referred to oxygen instead of to air.

The weight in grams of a liter of (chemically prepared) oxygen, under standard conditions,[4] has been determined by 13 observers, the mean value being 1.42893 with a total variation of approximately 2 parts in 10,000. Similar observations on the weight of a liter of CO_2-free dry air yield average values varying systematically from 1.29266 and 1.29284, for samplings at or near sea level, to 1.29301

[2] L. W. Tilton, B.S. Jour. Research, vol. 2 (RP64), p. 909–930, 1929; vol. 6 (RP262), p. 59–76, 1931; vol. 11 (RP575), p. 25–57, 1933.
[3] Erster Ergänzungsband, p. 160–163, 1927.
[4] A temperature of 0 C and a pressure of 760 mm of mercury (at 0 C, g=980.616) was used by E. Moles (Jour. de chim. phys., vol. 19, p. 100, 1921; Zeits. f. Phys. Chem., vol. 115, p. 61, 1925) in his critical review leading to the average value which was adopted for oxygen in the Landolt-Börnstein Tabellen.

and 1.29332 g for those made at altitudes of 700 and 1,960 meters, respectively. Also, as time varies at a single place of sampling, the total range of values obtained by a given observer is at least 5 and in some cases [5] 10 or 12×10^{-4} g; that is, from 2 to 5 times the variation among results by all observers on pure oxygen. Moreover it appears that these variations with time of sampling at given latitudes and altitudes are more or less systematically related to certain weather conditions existing at the time the sample is taken. In particular there is considerable evidence [6] to show that minima of density are often obtained on air sampled at or very soon after maxima of atmospheric pressure. It should also be mentioned that Paya and Moles [7] have made several weighings of atmospheric nitrogen and find similar but smaller systematic variations with pressure existing at times of sampling. In brief, it seems fairly well established that the bona fide time variations in the weight of a liter of CO_2-free dry air approximate 1 part in 1,000.

III. CHEMICAL ANALYSIS (CHIEFLY VOLUMETRIC)

Attempts have been made to explain the observed gravimetric variations as arising mainly from variations in the oxygen content of air. According to the Loomis-Morley [8] hypothesis, cold air which is less rich in oxygen should descend from upper regions during periods of high barometric pressure. Possibly atmospheric nitrogen should be less rich in argon when sampled under these same conditions. Important fluctuations at least as large as ± 0.2 percent oxygen (i.e., ± 1 percent of the oxygen content), together with ± 0.02 percent argon (i.e., ± 2 percent of the argon content), seemed required in order to explain the gravimetric data (including only the time variations and excluding those ascribed to altitude); but during the very early experiments in connection with this problem the variations in composition as found by chemical analysis were of a magnitude not altogether inconsistent with acceptance of this hypothesis.

1. OXYGEN CONTENT

The development of improved technique in volumetric gas analysis soon led, however, to a decidedly narrower range in the observed variations in composition, and the fluctuations in (averaged) oxygen content within the North Temperate Zone do not appear [9] to exceed ± 1 part in 1,000 volumes. They are scarcely ± 3 parts in 1,000 even if one considers both maxima and minima and includes the joint investigation by Morley, Hempel, and Kreussler on air collected simultaneously in 1886 at Cleveland, Bonn, Dresden, Para, and Tromsö.[10] Moreover, the greater normal densities found upon sampling at higher altitudes do not seem in accord with the Loomis-Morley hypothesis. The possible connection between such high densities and certain variations in atmospheric ozone, as suggested

[5] Recent data are given by A. Stock, H. Ramser, and G. Eyber, Zeits. f. Phys. Chem., vol. 163, p. 82–90, 1933.

[6] Ph. A. Guye, Jour. de chim. phys., vol. 15, p. 561–576, 1917; A. Jaquerod and Ch. Borel, Jour. de chim. phys., vol. 19, p. 11–28, 1921.

[7] M. Paya and E. Moles, Anales soc. españ. fís. y quím., vol. 20′, p. 247–254, 1922; 24′, p. 564, 1926.

[8] E. W. Morley, Amer. Jour. Sci., vol. 18, p. 168, 1879.

[9] M. S. Blanchard and S. F. Pickering, B.S. Scientific Papers, vol. 21 (S529), p. 167, 1926.

[10] For collected data and bibliography see F. G. Benedict, The Composition of the Atmosphere, publication no. 166 of the Carnegie Institution of Washington, 1912.

for the vicinity of Madrid,[11] may be untenable as a general and satisfactory explanation, not only because of the very small ozone concentrations that are usually found by direct tests but also because the presence at the earth's surface of the required amounts of from 0.01 to 0.02 percent of such an active agent as ozone should be chemically noticeable. If 20.94 ± 0.05 is adopted as the range in volume percentage of oxygen in CO_2-free dry air, then comparatively few reliable analyses on normal air are found in disagreement therewith. Those analyses made by Moles [12] on air sampled at Valencia and at Madrid are certainly exceptions. Possibly it is worth noting that Moles used a gravimetric method of analysis, whereas all air analyses considered by Blanchard and Pickering,[13] and also those made by Stock, Ramser, and Eyber,[14] were effected by volumetric procedures.

2. ARGON CONTENT

Very few direct determinations of argon in air seem to have been made. The writer has noticed those by Schloesing,[15] by Kellas,[16] and by Moissan.[17] A value of 0.936 ±0.003 percent is suggested as a range in good agreement with the evidence which they present.

3. HYDROGEN CONTENT

Concerning the proportion of hydrogen in the air it is well known that Rayleigh [18] and other investigators [19] have reported negligible amounts. On the other hand, Gautier,[20] whose work was quite elaborate but has received little notice, finds at least 2 parts of hydrogen per 10,000 of ocean air taken near sea level 40 kilometers off the French coast. Rayleigh considered Gautier's work as very carefully and thoroughly done and expressed his embarrassment and a temptation to suppress his own results. A hydrogen percentage of 0.01 ±0.005 seems, therefore, in fair agreement with these data and the range as thus expressed is probably ample.

4. NITROGEN CONTENT

If all constituents of CO_2-free dry air other than nitrogen, oxygen, argon, and hydrogen are negligibly small, it then follows from the estimates listed above that the range in nitrogen content is expressible as 78.114±0.058 percent. This, of course, is only indirect evidence for the nitrogen content of air and the range depends almost entirely on the variations that are found in oxygen. Unfortunately no constituent except oxygen has been satisfactorily investigated by numerous experiments over periods of time sufficiently long to reliably establish the constancy or variability in its volume percentage.

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[11] E. Moles, T. Batuecas, and M. Paya, Anales Soc. españ. fís. y quím., vol. 20′, p. 34–40, 1922. The fluctuations in density and in oxygen content that these observers find at an altitude of 685 meters are somewhat greater than have been found elsewhere (lower altitudes) since von Jolly's experiments at Münich (altitude 515 meters) in 1879.

[12] E. Moles, Gazetta chimica Italiana, vol. 56, p. 938, 1926.

[13] See footnote 9, p. 113.

[14] See footnote 5, p. 113.

[15] Th. Schloesing, Comptes Rendus, vol. 121, p. 525, 1895; vol. 123, p. 696, 1896.

[16] Alex. Kellas, Proc. Royal Soc. London, vol. 59, p. 66, 1896.

[17] H. Moissan, Bull. Soc. chim. de Paris, (3) vol. 31, p. 729–735, 1904.

[18] Lord Rayleigh, Phil. Mag. (6) vol. 1, p. 100–103, 1901; (6) vol. 3, p. 416–422, 1902, obtained results varying from negative values up to 6 parts of hydrogen per 100,000 of air with an average of approximately 3 parts per 100,000.

[19] G. Claude, for example, Comptes Rendus, vol. 148, p. 1454, 1909, finds less than 1 part of hydrogen per million parts of air. See also A. Krogh, Vidensk. Selsk. Math-fysiske Medd., vol. 1 (nr. 12), p. 1–19, 1919.

[20] A Gautier, Annales de Chimie et de Physique, (7), vol. 22, p. 5–110, 1901; Bull. Soc. chim. de Paris (3) vol. 29, p. 108–116, 1903.

Consequently, aside from the values for oxygen, the ranges suggested in the above summary are simply tentative estimates. Even for oxygen it seems possible that further work by gravimetric methods may lead to some revision.

IV. REFRACTOMETRIC EVIDENCE OF VARIATION

In comparison with densities and chemical analyses, direct optical measurements on air have been less frequently made. Nevertheless, since 1857 the index of refraction of dry air has been determined in at least 40 distinct series of experiments. The general average of these data [21] is, for sodium light, $\mu = 1.0002925_4$ at a temperature of 0 C and a pressure of 760 mm of mercury. Only 21 of these 40 values fall within $\pm 5 \times 10^{-7}$ of the mean, 11 values being lower and 8 higher than this range. Since these data have not hitherto been collectively analyzed it is appropriate to remark concerning their possible accuracy and significance.

1. ACCURACY OF THE DATA

It is, of course, true that many of these observers did not remove CO_2 from the air, but the total variations on that account can scarcely be as large as 1×10^{-7} in index. Also, various values of wave lengths are assumed and various values of gravity have been used (or neglected) in the corrections to standard pressure; but, with one or two exceptions, these uncertainties are likewise very small, being matters of approximately $\pm 1 \times 10^{-7}$ in index.

Sources of error that are of somewhat more importance are inadequate care in removing moisture, the use of different temperature coefficients of index of air, and perhaps the assumption that, even for low pressures, the rate of shift of interference fringes is constant as observed pressure varies uniformly. These errors, so far mentioned, do not affect μ directly, but have their proportionate influence on $(\mu-1)$ only. The effect of pressure on the apparatus is a different matter, not often explicitly considered, and the error in μ itself may be proportional to certain compressive changes in length. Fortunately, with some experimental procedures, for example with the Jamin interferometer which is the one most frequently used for these measurements, the compressibility error is effectually compensated by corresponding variation in the air paths outside the tubes. For the Fabry-Perot type of apparatus, however, it would seem that such an effect may be appreciable, although even here the error can be (as in the Meggers and Peters apparatus) reduced by a choice of

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[21] The Landolt-Börnstein Tabellen (fifth edition) list and give references to 27 of these values, the average for that restricted group as therein listed being 1.0002925_6. The other references are:
J. Jamin, Annales de Chimie et de Physique, (3) vol. 49, p. 282–303, 1857.
E. Mascart, Comptes Rendus, vol. 78, p. 617–679, 1874.
L. Magri, Physikalische Zeits., vol. 6, p. 629–632, 1905.
S. Loria, Annalen d. Phys. (4) vol. 29, p. 605–622, 1909.
I. M. Mathews, Jour. Franklin Inst., vol. 177, p. 673–686, 1914.
V. Posejpal, Annalen d. Phys. (4) vol. 53, p. 629–646, 1917.
V. Posejpal, Jour. de Phys. (6) vol. 2, p. 85–92, 1921.
A. Pérard, Procés-Verbaux des Séances, vol. X, p. 16, 1923.
A. Zwetsch, Zeits. f. Phys., vol. 19, p. 398–413, 1923.
Tausz und Görlacher, Zeits. f. techn. Phys., vol. 12, p. 19–24, 1931.
Sears and Barrell, Phil. Trans. Royal Soc. London, vol. (A) 231, p. 126–127, 1932.
Kösters und Lampe, result obtained in 1932 at the Phys. Techn. Reichsanstalt and privately communicated to the writer.
C. G. Peters, unpublished result obtained in 1917 at the National Bureau of Standards with apparatus different from that used by Meggers and Peters.

suitable separating posts and perhaps to some extent compensated by air film and certain differential compressibilities.

The writer has reviewed many of these observations and has applied tentative corrections in those cases where the necessary data are given or have been readily obtained. The general average of all values remained essentially unchanged by these corrections, however, and the only important individual changes are a possible reduction of 9×10^{-7} in Mascart's (second) result[22] and an increase of 5×10^{-7} in index after reanalyzing and applying the Mascart index-pressure equation to the data given by Chapuis and Rivière.

2. CHARACTER AND SIGNIFICANCE OF THE VARIATIONS

If the variations among all of these indices of air could reasonably be considered as accidental errors in measurements, the mean could probably be accepted as establishing the refractivity of air within a very few units of the seventh decimal place. Some careful workers have, however, obtained results that differ from the mean by amounts that materially exceed the estimated errors. In particular, Lorentz (1870–75), Scheel (1906), and Meggers and Peters (1917) give values which are lower than the mean by 15, 9, and 8×10^{-7}, respectively, while Ketteler (1865) and Quarder (1924) find results which are high by 22, and 7×10^{-7} in index. In this connection it should be remembered that air is compared with vacuum in these measurements and that differences of $\pm 10 \times 10^{-7}$ in refractive index correspond to variations as large as ± 1 part in 300 in the quantity actually determined, namely the (excess) refractivity, $\mu-1$. In view of these facts and the known variations in air density, it appears possible that a similar uncertainty of approximately $\pm 1 \times 10^{-6}$ may exist in the index of refraction of air.

If the index of air varies slowly to this extent then it is easily shown that relative indices of refraction of very dense glass cannot (over a period of several years) be redetermined or checked with a precision better than $\pm 2 \times 10^{-6}$. If, in addition, these variations should prove to be functions of daily meteorological conditions some further question would arise concerning possible fluctuations of similar magnitude in index over relatively short periods of time. Recently, however, it has been reported [23] that measurements made on μ at the Reichsanstalt to 1×10^{-8} show no noticeable vacillations with meteorological conditions, and this result is in agreement with the constancy which Stoll [24] found in his precise experiments at Zurich.

Any uncertainties in index of refraction of air are of great importance, moreover, in correcting to vacuum values all wave lengths that are measured in air. An error of 1×10^{-6} in index of air corresponds to an error of 0.005 A in such a correction for a wave length of 5,000 A. Standard wave lengths are often given to 4 decimals and it was, no doubt, this state of affairs that in 1931 prompted a Subcommittee of the International Committee on Weights and Measures to sponsor further work on the refractivity of air.

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[22] This is chiefly a temperature coefficient correction. Analysis of Mascart's data indicates that his temperature investigation was systematically in error when data were taken at other than room temperatures. On the other hand, Perreau, who afterwards used the same apparatus, considered Mascart's result as independent of Mascart's value for the temperature coefficient.

[23] Kösters and Lampe, Zeits. f. Instrumentenkunde, vol. 35, p. 201–2, 1933.

[24] E. Stoll, Annalen d. Phys. (4), vol. 69, p. 81–111, 1922.

V. QUANTITATIVE DISCUSSION OF COMPOSITION AND CONSTITUTION OF AIR

The variations evidenced by gravimetric, volumetric, and refractometric data can now be readily compared. Using the percentages adopted in section III, and taking the means of published [25] values for the densities and refractivities of the various constituents of CO_2-free dry air, some interesting computations can be made (by the additive rule for gaseous solutions) concerning the possible variations in these properties for atmospheric nitrogen and for air itself. The results are given as table 1 and the arrangement is such that the entries therein are self-explanatory. The most important result of these computations is the conclusion that known variations in the chemical composition of air, while they are sufficiently large to account for some [26] of the known variations in the normal density of air, are wholly inadequate to cause any appreciable variation in the refractivity of CO_2-free dry air. Even ozone, in amounts up to 0.02 percent can only cause variations beyond the seventh decimal place of the refractive index of air.

TABLE 1.—*Composition, density, and refractivity of CO_2-free dry air under standard conditions (see footnote 4, p. 112)*

Chemical substance	Percentage composition by volume (based on published data)		Density (mg per liter)		Refractivity $(\mu_D-1)\times 10^6$	
	Average	Normal variation	Average from published data	Net weight equivalent of normal variation in composition	Average from published data	Net refractivity equivalent of normal variation in composition
N_2	78.11_4	−0.058 / [1] +0.048	1,250.52	+0.025 / −0.020	297.8	−0.0034 / +0.0028
O_2	20.94	±0.05	1,428.93	±0.068	270.9	∓0.0105
A	0.93_6	±0.003	1,781	±0.015	282	∓0.0003
H_2	0.01	±0.005	90	∓0.060	140	∓0.0076
O_3	0.00	(+0.01)?	2,220	(+0.093)	519	(+0.0227)
Air	Computed from above		1,292.73	+0.26 / −0.16	292.0	+0.04 / −0.02
	Average of published observations.		[2] 1,292.75	±0.5	292.5	±1
Atmospheric nitrogen	Computed from above: Including H_2		1,256.65	±0.10	297.6	±0.01
	Neglecting H_2		1,256.80	±0.03	297.6	±0.003
	Average of published observations		[2] 1,256.67	±0.10	----------	----------

[1] Considering the ozone variation as tabulated herein.
[2] Near sea level.

In this connection, however, the isotopes of oxygen and of nitrogen may require consideration. Recent measurements [27] have shown that the ratio of O^{18} to O^{16} is approximately 1: 630 and the ratio of N^{15} to N^{14} seems to be almost twice that value.[28]

[25] The Landolt-Börnstein Tabellen have been used as the principal source for these data. For argon see also E. Moles, Ber. Deutschen Chem. Gesellschaft, vol. 60, p. 134–138, 1927.

[26] In general it may be said that, excluding ozone, all other variations in chemical composition that appear possible in view of accumulated (volumetric) chemical data do not explain more than 30 percent of the established density variations. Moreover, +0.01 percent ozone can account for only 10 percent of the increases in density even if unaccompanied by a depletion of O_2.

[27] H. Kallmann and W. Lasareff, Zeits. f. Physik, vol. 80, pp 237–241, 1933.

[28] G. M. Murphy and H. C. Urey (Phys. Rev., vol. 41, pp 141–148, 1932) find 1 : 346 for the ratio N^{15} to N^{14}.

The possible presence of oxygen in the forms $(O_2)_x$ must also be remembered,[29] particularly in connection with the reported increased normal densities of air sampled at higher altitudes. Perhaps the degree of existing association may be influenced by various meteorological conditions.

Presumably then a change in the rate of general stirring and mixing of the atmosphere could produce changes in density, and probably in refractivity, that would exceed those predictable from data given by the purely (volumetric) chemical methods of analysis which of late have been used almost exclusively in investigations of this problem. On the other hand, gravimetric methods of analysis would, of course, be sensitive to variations in molecular association and in ratios of isotopes. This may partially account for the agreement that Moles [30] finds between fluctuations in density and those in composition; also for the fact that Stock, Ramser, and Eyber,[31] who used a volumetric method, do not find such an agreement.

Unfortunately no refractivities of the isotopes of oxygen and nitrogen are as yet available for computations concerning these questions. Insofar as density [32] is concerned it is readily shown that variations of $\pm$ 10 or 15 percent in the above-mentioned ratios of these particular isotopes of oxygen and nitrogen would cause variations of ± 0.03 or 0.04 mg in the weight of a normal liter of air, that is, only 6 or 8 percent of the established density variations with time in a given locality.

VI. REFRACTIVITY AND SUNSPOT NUMBER

With these general ideas in mind, the data on refractive indices of air as determined by various observers were examined with particular reference to the time sequence in which the observations were made. Considering only the data published in the last two decades it was at once evident that 8 of a total of 10 values obtained between the years 1912 and 1923 were lower than the general average (of $\mu_D = 1.0002923_7$) for the 20 years, while 8 of the 9 subsequent values have equaled or exceeded the general average. It happens that these 2 groups lie within the 2 opposite phases of the current 23-year magnetic cycle of sunspots. Consequently, since degree of storminess of the earth's atmosphere (at least in North America) has been correlated [33] with the Wolf-Wolfer series of annual relative sunspot numbers, and since sunspot numbers were appreciably higher during the first half of this 23-year period, a partially explainable correlation between sunspot number and variations in the refractivity of air was suggested. For the 19 indices determined between 1912 and 1932, and for the corresponding sunspot numbers, computation gave a Pearson correlation coefficient,[34] $r = -0.52$ (± 0.11 probable error), and this preliminary result has been published.[35]

[29] Oliver R. Wulf, Phys. Rev., vol. 41, pp 375–376, 1932, discusses the presence of O_4 in the atmosphere and its effect on the formation of O_3 in the lower air at moderately high altitudes.

[30] See footnote 12, p. 114.

[31] See footnote 5, p. 113.

[32] This reference to densities should not, of course, be construed as relevant evidence concerning refractivities. For example, it is readily seen from the data of table 1 that both oxygen and argon are denser than either nitrogen or air but have lower refractive indices.

[33] Ellsworth Huntington, Earth and Sun, p. 29; Yale University Press, 1923. See also the Julius Hann Handbuch der Klimatologie, 4th ed., p. 406, 1932; and Shaw's Manual of Meteorology, vol. 2, p. 336.

[34] See any text on the theory of statistics.

[35] L. W. Tilton, Nature (London), vol. 132, p. 855, 1933.

1. AVERAGE REFRACTIVITY DURING MAGNETIC CYCLE OF SUNSPOTS

In the present examination of all available data on the refractive index of air it was assumed that the "double sunspot periods" 1844 to 1866, 1867 to 1889, and 1889 to 1911 are comparable with the present magnetic cycle from 1912 to 1934 and in each of these 4 cycles the years were numbered from 1 to 23. Each observed index of air was then tabulated in one of 23 columns as determined by the date of first publication or by a more precise date if such has been noticed.[36] In order to simplify the presentation and the discussion, and also to avoid the element of personal choice, no instrumentally determined absolute values published since 1857 have been intentionally rejected and results have been used as they are computed and published by the observers.[37]

In obtaining values of the index for the sodium lines, the computed rather than the observed values have been favored, provided there are accompanying dispersion equations which seem reliable; and necessary interpolations have been made with such equations. All extrapolations and some interpolations have been made by comparison between the observers' data and those computed by the Meggers and Peters dispersion equations which are based on observations for a very large number of wave lengths. Where temperature reductions have been necessary they have been made by the Meggers and Peters coefficients which, for lines near the middle of the visible region, are approximately equal to averages from the work of Benoit and of Pérard, both of whom observed at a large number of temperatures between 0 and 100 C.

Simple averages were formed in each of the 23 columns in which indices were tabulated and then these results were plotted in figure 1 for comparison with the Wolf-Wolfer series of annual relative sunspot numbers, which were similarly averaged over the 4 magnetic cycles of 23 years each. Each plotted point depends on from 1 to 5 series of experiments as indicated by the numbers shown near the small circles. No experiments occurred in the years 1, 2, 3, 9, or 10 of any cycle.

Similar attempts to compare sunspot numbers and refractive-index data over a single or 11-year sunspot period are not quite as satisfactory as for the double or 23-year cycle which has been used. It seems, at least for the current cycle from 1912 to 1934, that those factors which tend to produce low refractivity during high sunspot numbers are not so potent during the second half of the double period, or else that their effect is masked. This, of course, may mean that two distinct causes having different periodicities are operating to produce the observed variations in refractivity.

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[36] For example, L. Lorentz, publishing first in 1875, states that his experiments on air were begun in 1870 and often repeated through the years because he obtained such a low value. His result has been tabulated as of 1872. Benoit, in 1889, gives dates from July 1882 to January 1883. Stoll, in 1922 (see footnote 24 p. 116), lists some data as of 1920 and says his experiments were in progress when the Meggers and Peters paper appeared. (That paper was issued in October 1918 and appeared in B.S. Bulletin as of July 1919.)

[37] A similar analysis based on selected and corrected data has been carefully considered but in most instances and in all general respects there is insufficient difference in final results to justify detailed presentation. In the case of data by A. Zwetsch, however (see footnote 21, p. 115), his "corrected" value has been ignored in favor of the uncorrected value which he himself lists as comparable with those of other observers. Dickey's results cannot be used because of the large arbitrary correction which he applies to all his data after a comparison with indices given by certain other observers.

2. NORMAL RANGE IN REFRACTIVITY AND A STATISTICAL CORRELATION

The points plotted in figure 1 suggest a normal range in refractivity between upper and lower limits such as those which have been sketched above and below all the points. Certainly a curve of average

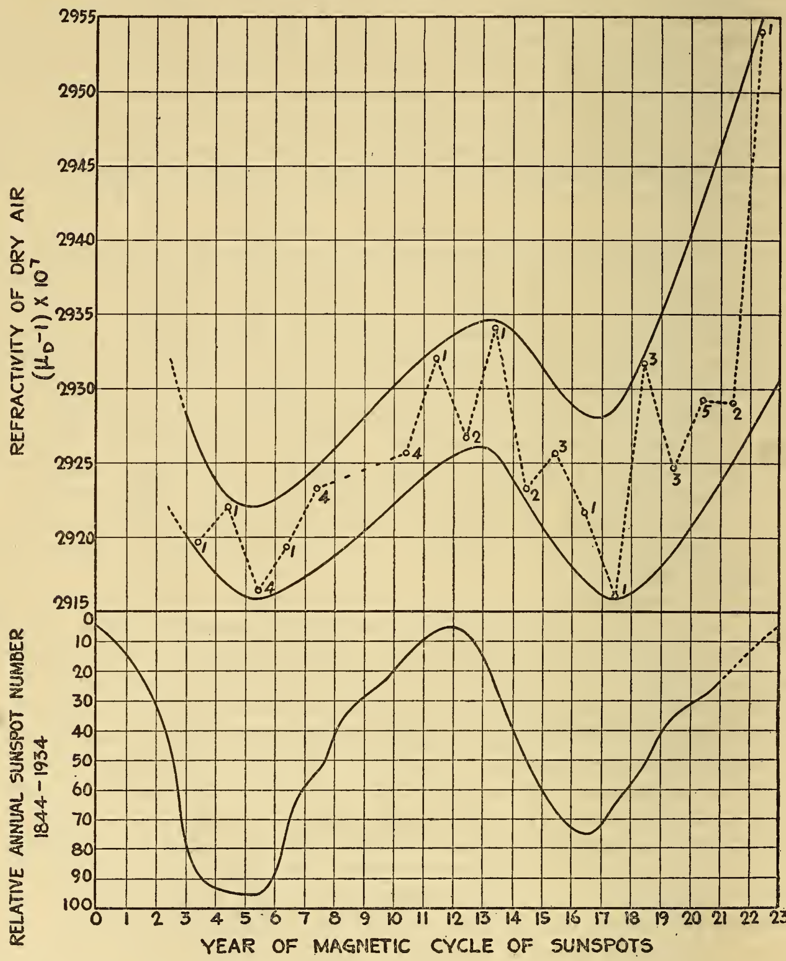

FIGURE 1.—*Average refractivity of dry air (at 0 C and 760 mm pressure) compared with average of sunspot numbers.*

The interval 1844 to 1934 has been divided into 4 periods of approximately 23 years each. The figures near the small circles indicate the number of experimental results that are available for averaging as of corresponding years during any of the 4 cycles. No experiments occurred in the years 1, 2, 3, 9, or 10 of any cycle. For the years 22 and 23 only 3 values of annual sunspot number are available for estabilshing the curve of average sunspot number (Wolf-Wolfer series).

refractivity is remarkably similar to that of average sunspot number but it must be remembered that some of the individual results depart widely from the averages, both for index and for sunspots. Consequently, in order to investigate further the matter of a normal range in refractivity the individual values were plotted in figure 2 for a

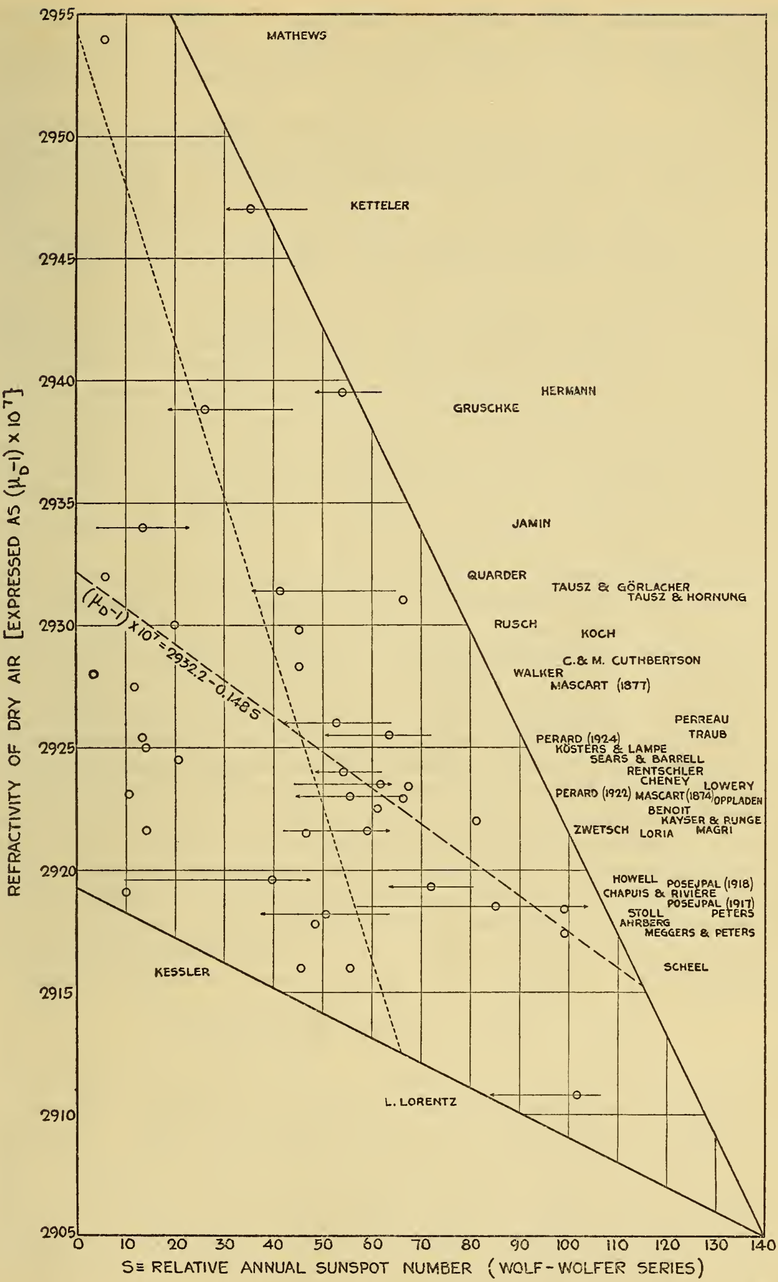

FIGURE 2.—*Correlation between refractivity of dry air and sunspot number.*

The Pearson coefficient of correlation is $r=-0.48$ (±0.08 probable error) as determined from 40 pairs of values. Except where the magnitude and direction of annual change in sunspot number is indicated by arrows, the uncertainty in determining such number is estimated as ±6 or less. Note that all observations are located in a triangular area having the broad base $\mu_D=1.000292$ to 1.000296 for $S=0$ with the apex near $\mu_D=1.000290_5$ for $S=140$ which is the upper limit for the whole period from 1844 to 1934.

direct comparison with sunspot numbers. In this latter exhibit arrows have been drawn to show the change in solar activity during a period (usually 1 year) within which an experiment is not definitely dated.

It should be noted that the lowest value of index was reported by Lorentz and that he began his work in the year of largest annual sunspot number which has been observed since 1778. Miss Mathews, on the other hand, who reports the highest value on record is the only observer who has taken data during the last year of a 23-year cycle. Ketteler reported the next highest index in 1864 which was the 21st year of a cycle.

All of these data are distributed over a triangular region forming considerably less than half the total area of figure 2. This particular distribution suggests that during the "disturbed periods", at times of high sunspot number, the index of refraction of air is relatively low and approaches a fairly constant value, the range being approximately 1.000291 to 1.000292. During the "quiet periods", when sunspot numbers are low, the index is higher and there may be a much wider variation with a normal range extending from 1.000292 to 1.000294 or higher, depending perhaps on the elapsed time since marked atmospheric disturbances.

Computation gives a Pearson correlation coefficient, $r=-0.48$ with a probable error of ± 0.08; and the characteristic (or regression) lines have also been determined and are shown in figure 2. Although this value of r is not particularly high (as compared with unity for perfect correlation) it suggests a degree of relationship far from negligible. The value of r approximates six times that of its probable error and thus it is rather improbable (say 1 in 10,000) that the apparent degree of systematic trend in refractivity can be entirely the result of chance. This result for all data taken since 1857 (40 series of experiments) is in very close agreement with the previously mentioned correlation ($r=-0.52$) based on the data since 1912. The slope of -0.15 for the line of estimated refractivity for the 4 cycles of 23 years each is large compared with -0.08 which was previously[38] found for the current cycle only. This may, of course, be attributed in part to a coincidental irregularity in certain of the older measurements, but it suggests that the current cycle has not included times of extreme conditions.

VII. CONCLUDING DISCUSSION

Before concluding, brief references should be made to variations in the measurements of the dielectric constant of air and to determinations of absolute wave lengths which have been made in air. In regard to the dielectric constant, it seems that the number of observations and the accuracies obtained do not warrant a detailed analysis. The value given in the International Critical Tables is $1.000585 \pm 5 \times 10^{-6}$ and from theory and the conclusions reached in this paper a variation of about $\pm 2 \times 10^{-6}$ would be written to express the necessary minimum range in values for this constant.

If the index of refraction of air varies as suggested by this analysis of existing data, then all determinations made in standard dry air on the relationships between wave lengths of light and other standards

[38] See footnote 35, p. 118. For estimating refractive indices of air during the current cycle, 1912 to 1934, the previously published provisional equation $(\mu_D-1)\times 10^{-7}=2927.5-0.079S$ is probably preferable to the equation given in figure 2, for the complete interval since 1857.

of length are subject to a periodic error, having an amplitude of about ±1 part per million. In the limited amount of published data concerning these relationships, the agreements are better than this estimate of the possible discrepancies but further consideration [39] shows that this should be the case, since no experiments of this nature have been conducted at such times that extremes in the average refractivity of air would necessarily be expected according to the curves of figure 1.

When considering refractivity as a possible function of general turbidity (on a large scale) and subsequent very gradual settling, it must be remembered that changes in the oxygen and argon volume content of air are not important because their optical densities differ but little from that of air, the small changes in refractivity being, in fact, of opposite sign to those produced in density (m/v). On the other hand, until something more is known regarding the relative proportions and refractivities of the various isotopes and associated molecules which may be present in air, it seems impossible to say that appreciable variations in the index of air may or may not be occasioned by simple storminess and turbidity of the atmosphere, and the subsequent gradual settling of certain components which are heavier and also have higher refractive indices.

The apparent time lag required for the highest indices seems to favor such views as compared with some electrical hypotheses relating to changes in refractivity. Moreover, the excellent consistency between the individual values in Stoll's series of measurements, and the recent report regarding the constancy of air indices obtained at the Reichsanstalt [40] do not accord with certain electrical considerations (such, for example, as an appreciable change produced at low altitudes in the degree of association of molecules), because data on other electrical and magnetic conditions usually show pronounced variations over short periods of time. The views herein presented do not seem, however, to conflict with the possibility that some electrical hypothesis (perhaps increase in ionization) may account in part for those small decreases in the apparent normal density of air that are often found if samplings follow rather promptly after sudden increases in barometric pressure.

All of the experimental evidence, considering both density and refractive index, does accord with the possibility of a small electrical, magnetic, or ultraviolet light effect (say, by means of a change, produced more effectively at increased altitudes, in the degree of association of molecules) which may increase with altitude but is otherwise relatively constant in value except for a slight 23-year variation which is superposed on the 11-year cycles of storminess.

In any event it appears unsafe to rely on the constancy of μ, the refractive index of air, over a period of years, or even when sampled simultaneously in different regions. The average of all measurements, namely 1.0002925 at 0 C and 760 mm pressure, still appears to be a

[39] For example, Benoit, Fabry, and Perot (Travaux et Mémoires du Bureau int., 15, p. 1–134, 1913) observed in 1906, the 18th year of a cycle, and the Sears and Barrell (see footnote 21, page 115) provisional values were obtained in 1931, the twentieth year of the present period.

[40] See footnote 23, p. 116. Presumably this refers to constancy over a relatively short period as compared with the very long times required for appreciable segregation by settling out of heavier components.

fair general value for the sodium lines index, but it may be preferable for any given year to estimate the index from the equation

$$(\mu_D - 1) \times 10^7 = 2932.2 - 0.148S \qquad (1)$$

where S is the relative annual sunspot number according to the Wolf-Wolfer series of sunspot observations and the constants are provisional values derived from all available data taken since 1857. The probable error of the estimates derived from this equation is $\pm 5 \times 10^{-7}$.

Since the annual sunspot numbers commonly vary from 0 to 100 it appears from equation 1 and its probable error that variations in index of air may frequently extend over a range of about $\pm 12 \times 10^{-7}$ from the average value. Consequently, since $n = \frac{\bar{n}}{\mu}$ is the definitive relation between the relative index, n, of a medium and its absolute index, $\bar{n}$, one may write, $\Delta\, n = \pm 12n \times 10^{-7}$ to express approximately the corresponding uncertainty frequently present in carefully corrected indices of refraction which in the course of years are measured with respect to the CO_2-free dry atmosphere of the earth. Similarly, it is found that this same degree of uncertainty in air index is approximately equivalent to ± 0.4 percent variation in the 4 and 5 figure values of $(\mu\lambda - \lambda)$ which are tabulated and used in correcting wave lengths from air to vacuum values. Obviously, then, this question of possible variability in the optical density of air should receive careful consideration whenever one discusses the subject of defining or using radiation in air as a standard of length. The uncertainty can be avoided if such a standard is defined and used in vacuum but with air involved it seems that further experiments over a period of years should precede international agreements.

WASHINGTON, February 20, 1934.